

Chemical Structure of Heavy Oils Derived from Coal Hydrogenation by Mass Spectroscopy

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Introduction

Coal hydrogenation heavy oil consists of numerous complicated hydrocarbons and nonhydrocarbon compounds, consequently the elucidation of the chemical structure is extremely complicated and time consuming. Thus, the chemical structure of coal liquids have been investigated mainly to the present by means of ^1H - and ^{13}C -NMR techniques or a combination thereof. In other words the technique of mass spectrometry for structural analyses is advantageous to gain information of the individual compounds regarding molecular weight and compound types [1,2]. A combination of dual-packed adsorption liquid chromatography (LC) and gel permeation chromatography (GPC) developed by the Bureau of Mines API project 60 [3] for separation into compound types and further into their molecular size are appropriate to the sample preparation procedure for mass analyses, because molecular coefficient were assumed to be approximately the same for LC-GPC sub-fraction inasmuch as they have characteristic compound types and narrow molecular weight distribution. On the other hand, results of GPC technique which is a very useful method to clarify complicated mixtures of heavy oil derived from coal, was compared to the mass results. It can be concluded that both results from mass and GPC analyses should be used independently to elucidate the chemical structure of coal liquids.

Experimental

Sample preparation of heavy oil

Hydrogenation reaction of Hiawatha, Utah coal (C: 72.0, H: 5.6, N: 1.7, S: 0.90, O: 19.8, d.a.f.%) was performed with the condition of 950°F of reaction temperature and 1800 psi of hydrogen pressure with ZnCl_2 impregnated to coal as catalyst by an entrained-flow tubular coil reactor of the University of Utah process [4]. The reaction products were trapped in three reservoirs connected to the reactor in series and was separated according to their condensability. Heavy oil products collected in the first reservoir nearest to the reactor was subjected to investigation in this work. Separation procedures to characteristic materials prior to gaining acid-base-less neutral compounds were described in our previous reports [5] and also shown in Fig. 1. Neutral heavy oil obtained was separated subsequently into compound types of saturated hydrocarbons (Fr-P), mono-aromatic (Fr-M), diaromatic (Fr-D), three and more large aromatic rings (Fr-T) and polyaromatic-polar compounds by means of dual-packed silica alumina adsorption liquid chromatography modified partially the Bureau of Mines API-60 method, with an additional solvent of 70% benzene-30% cyclohexane system to obtain separately a narrow cut of concentrate of 3 and 4 aromatic ring compounds. Elution curve of liquid chromatography are shown in Fig. 2. Respective type compounds Fr-M, D and T were separated further by GPC packed Bio-beads S-X4 and 8 according to their respective molecular size into 7 fractions. In Fig. 3, GPC elution curves for Fr-M, D and T were shown.

Mass spectra were measured by Hitachi M-52 GC-MS spectrometer. Mass spectra of each series of GPC subfraction for Fr-M, D and T were analyzed with the low resolution and low ionization voltage method by GC-MS technique for Fr-M-3 to 7 and Fr-D-3 to 7 and by direct insert technique for high molecular fraction of

Fr-M-1, 2, Fr-D-1, 2 and Fr-T-1 to 7, respectively.

Mass spectrometry was scanned repeatedly with 6 or 10 sec. interval times during the period of elution from GC column or volatilization of samples introduced into the ionization chamber and multiple mass spectra of about 50 to 800 for respective LC-GPC subfraction were measured to obtain the representative gross mass spectral data for complicated mixtures. Numerous mass spectra were treated by computer (Hitachi, HITAC 10 II) for the summing up of these spectra to calculate them as an integrated mass spectra.

Results and Discussion

Each series of LC-GPC subfractions were investigated previously for chemical characterization by ^1H - and ^{13}C -NMR method [6,7] and were elucidated to have approximately mono-, di- and tri- and/or tetraaromatic derivatives for Fr-M, D and T, respectively, as the average structural unit. It was also confirmed that values of aromaticity for GPC subfractions of individual compound types increase gradually with the increasing GPC fraction number from 1 to 7 and have also the largest fa values for Fr-T and the smallest one for Fr-M at the same elution volume of GPC. From the results described above, the separation effects of LC and GPC according to compound types and molecular size were assumed to be excellent. Considering these characteristics for chemical structure, LC-GPC subfraction are found to be suitable as samples for mass analyses because the molecular ion coefficient is not so large in difference among respective compounds in the same fraction.

Integral mass spectra of LC-GPC subfraction

On the measurement of mass spectra by means of the low energy ionization method, species of ion peaks observed were mostly parent ion and isotopic ion ($\text{P}+1$) and were minor for fragment peaks like ($\text{P}-1$), indicating that the cleavage of molecules are minor. Although, Fr-D-1 and Fr-T-1 which are the highest molecular weight in that they have large aliphatic substitution, were observed in the predominant fragment peak of odd mass number at lower mass range, therefore the data of these fractions were not included in this report. On the integral mass spectra of series of LC-GPC subfraction, the average number molecular weight were calculated from the mass to charge ratios (M/e) for respective parent peaks and those intensities, and are shown in Fig. 4. By increasing the fraction numbers of GPC for each compound type series, the molecular weight diminishes progressively from about 400 or 500 to 200 in proving the satisfactory fractionation of GPC. In Fig. 4, molecular weight results derived from vapor pressure osmometry were compared with the results of mass analyses to ensure the accuracy of conventional methods. The correlation between both are excellent except for a slight deviation from the theoretical line with the increase in molecular weight.

Compound types of LC-GPC subfraction

Deficiency of hydrogen number for M/e of parent peak can be predicted the type of compound by assigning the value of z number. Assuming that molecular ion coefficients are approximately similar, the contents of respective type compound for GPC fraction 1 or 2 to 7 of Fr-M, D and T were estimated semiquantitatively. Consequently, hydrocarbon types for Fr-M-1 to 7 were assigned mainly to alkylbenzenes ($Z=-6$), alkylmononaphthenobenzenes ($Z=-8$) and alkylindaphthenobenzenes ($Z=-10$) and for Fr-D-2 to 7 to alkyl-naphthalenes ($Z=-12$), alkylmononaphthenonaphthalenes ($Z=-14$) and alkylindaphthenonaphthalenes ($Z=-16$) and for Fr-T-2 to 7 to alkylphenanthrene or alkylanthracene ($Z=-18$), alkylpyrene ($Z=-22$), alkylcrysene ($Z=-24$) and these naphthenologs ($Z=-20$, -26). Distribution of various compound types for Fr-M, D and T in summing the contents of respective GPC subfraction 1 to 7 were shown in Fig. 5.

Alkyl carbon distribution

The same Z values in the integrated mass spectra for individual LC-GPC subfraction were selected to obtain the distribution of alkyl carbon in respective hydrocarbon types. In Fig. 6, the content distribution of molecular weight or alkyl carbon number on the same Z values were plotted for Fr-M, D and T series.

These ranges of alkyl carbon numbers move progressively from low to higher ones with 5 to 10 carbon extents in proceeding to GPC fraction 7 to 1 for respective hydrocarbon types. Therefore, separability of GPC for various hydrocarbon types was confirmed further by mass analyses as to be divided satisfactorily according to molecular sized especially by alkyl carbon number on these samples. It can be seen that Fr-M consists of larger alkyl carbon substitution which reaches 35 carbons for Z=-6 series, indicating a lower aromaticity and decreasing of Z values which indicates an increase of naphthene ring, distribution of alkyl carbon decrease. On the other hand, alkyl carbon number of Fr-T have a range of 0 to 10 indicating a lower aromaticity which is in agreement with the results from $^1\text{H-NMR}$ structural analyses.

GPC correlation for molecular weight vs elution volume

To predict the molecular weight distribution and chemical structure from the GPC elution curve, the GPC correlation curve between molecular weight and elution volume for corresponding structural compounds are necessary. However, it was very difficult to gain information of these relations because the supply of reference sample were limited. If the coal liquid itself can be used as a reference compound for calibration, useful GPC correlation of various compound type can be obtained. Molecular weight at maximum distribution by difference of alkyl carbon number for each GPC fraction on respective Z series shown in Fig. 6 were compared with elution volume for corresponding fraction. The correlation between the two were shown in Fig. 7. The relationship between the two for respective Z values on Fr-M, D and T are in fair as GPC correlations.

Molecular weight distribution for whole samples of Fr-M, D and T were constructed by summation of peak intensities for parent peak belonging to the same Z series corresponding to all GPC fractions, and were shown with the solid lines in Fig. 8. On the other hand, GPC elution curves for Fr-M, D and T were cited again in the same figure for comparison. The results from mass analyses for Fr-D and T do not include the data of Fr-D-1 and Fr-T-1 because of uncertain results of mass analyses for these as described previously, therefore a slight discrepancy were recognized in the vicinity of high molecular range. Although, considerable agreement between both derived from different methods are satisfactory.

References

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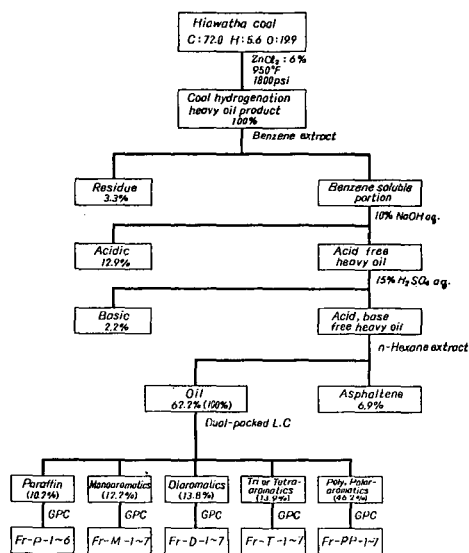


Fig. 1 Separation scheme

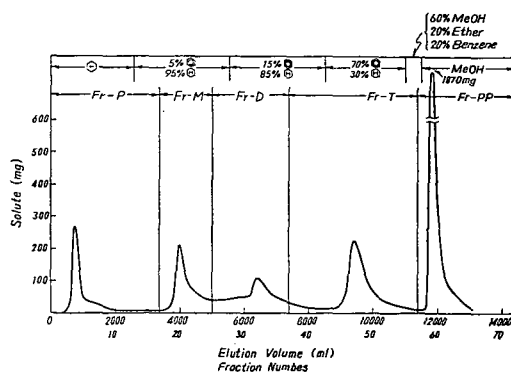


Fig. 2 Elution curve of dual-packed liquid chromatography

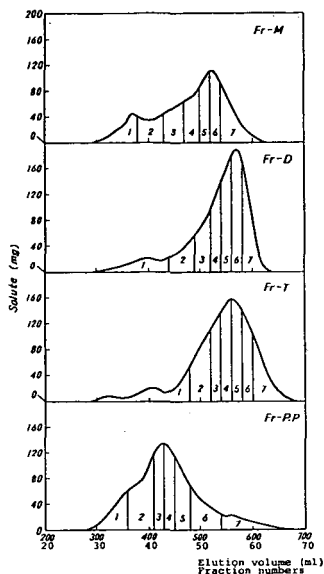


Fig. 3 GPC chromatogram of Fr-M, Fr-D, Fr-T and Fr-PP

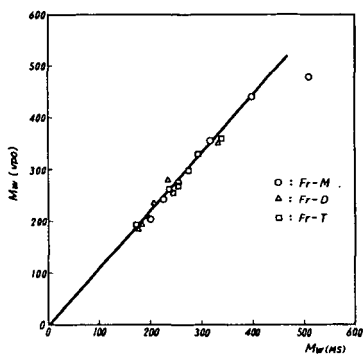


Fig. 4 Molecular weight results from VPO and Mass spectrometry

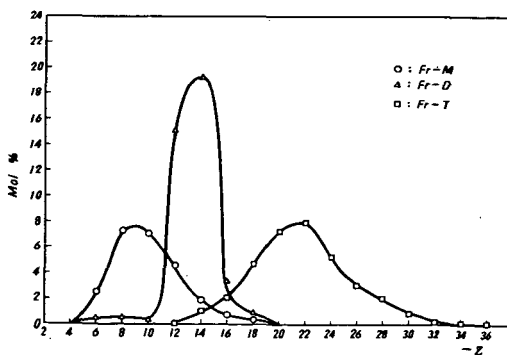


Fig. 5 Distribution of hydrocarbon type compounds for LC-GPC subfractions

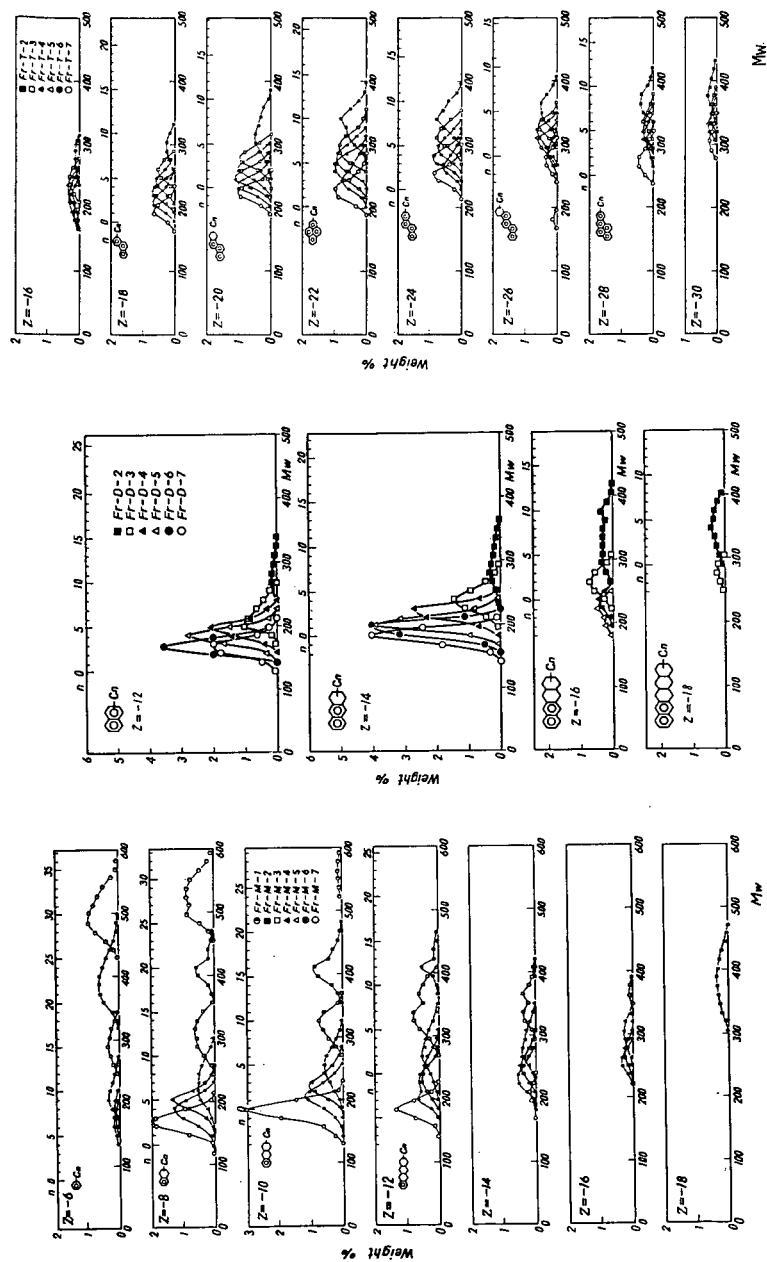


Fig. 6 Distribution of hydrocarbon compound types for Fr-M, Fr-D and Fr-T

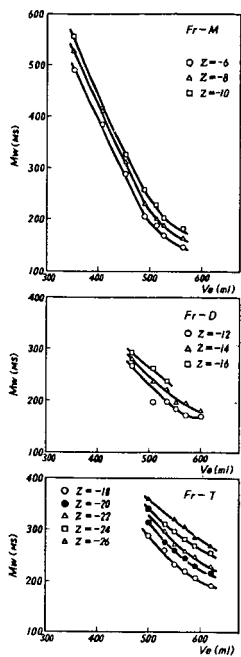


Fig. 7 Relationship between molecular weight and elution volume for various type of compound

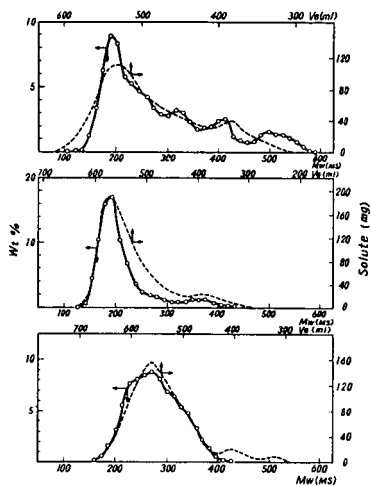


Fig. 8 Comparison with molecular weight distribution and GPC elution curves